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Coverage dependence of the electronic structure of chlorine adatoms on metal surfaces

H. Ishida

Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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The adsorption of Cl on metal surfaces is studied by a first-principles electronic-structure calculation within the local-density-functional theory as a function of adatom coverage (Θ). Hexagonal Cl layers with varying lattice constants are used as adlayers, and the substrate is modeled by the semi-infinite jellium. The work-function change, saturation Θ for the adsorption, and the role of metal substrates for these electronic properties are studied through analyses of the calculated charge density, total energy, bond-order, and adatom density of states.

The adsorption of Cl on metal surfaces is an important subject in surface science because of its role as "poison" in catalysis as well as for understanding the initial stage of corrosion and etching processes.[1-7] Since the molecular bonding of Cl_2 is weaker than the Cl-substrate bonding, the Cl_2 molecule dissociates on most metal substrates, leading to an atomic Cl adlayer. The adlayer is disordered at lower Θ, while ordered structures such as $c(2\times2)$ and $(\sqrt{3}\times\sqrt{3})R30°$ are formed on fcc and bcc metals at higher Θ. The multilayer formation does not take place at room temperatures, and a compressed atomic monolayer of Cl is completed at the saturation Θ (Θ_s), although a continued exposure to high-pressure Cl_2 gas sometimes leads to formation of bulk metal halides such as AgCl (Ref. 1) and $PdCl_2$ (Ref. 2). One very interesting observation is that the nearest-neighbor Cl-Cl distance at Θ_s is fairly insensitive to metal substrates; for example, it is 3.61, 3.60, 3.45, and 3.4–3.5 Å for Cu(001), Ni(111), Fe(001), and Cr(011) surfaces, respectively, in spite of the different lattice structures of these adlayers.[3-6] The above values, which are close to the diameter of Cl^{-1} (3.62 Å) and much larger than the bond length of Cl_2 (1.99 Å), were interpreted such that Cl adatoms are negatively ionized. The charge transfer from the substrate to Cl estimated from the adatom dipole moment was, however, typically only 0.1–0.2 electrons. For most substrates, the work function $\Phi(\Theta)$ continues to increase with Cl dosage almost linearly up to near Θ_s.[2-6] This is in contrast to the case of alkali-metal adsorption where the work-function decrease exhibits a clear maximum at around half a monolayer Θ.[8]

Halogen adsorption has not been studied theoretically so much as compared with the vast amount of experimental work. There are a number of slab and cluster calculations for Cl/Ag(001) and Cl/Cu(001) which focused on determination of the absorption site and the Cl-Ag (Cl-Cu) distance for the observed $c(2\times2)$ structure.[9-12] The electronic structure of Cl in the low-Θ limit was studied by Lang and Williams with their "adatom-on-jellium" model.[13] The aim of the present work differs from those in the above-mentioned studies. Instead of concentrating on a fixed Θ value, we clarify the electronic structure of Cl adatoms systematically as a function of Θ. The key parameter is the ratio of the strength of the Cl-Cl interaction to that of the Cl-substrate interaction. The Cl-Cl interaction comprises both the indirect dipole interaction and the direct orbital overlap among Cl atoms. The linear change in $\Phi(\Theta)$ and constant sticking probability of Cl_2 up to near Θ_s may imply that the Cl-Cl interaction is not important for lower Θ. However, it should play a central role in the electronic properties near Θ_s. Based on a first-principles calculation for Cl adlayers on a metal substrate, we study the work-function change, saturation Θ, and the role of metal substrates on these electronic properties.

Our model is an extension of the well-known work of Lang and Williams[13] on finite Θ values. We calculate the electronic structure of Cl adlayers on the semi-infinite jellium surface nonempirically, following the method of Ishida.[14] The method is fully three dimensional, and the semi-infinite calculation is performed by use of the embedding method of Inglesfield.[15] We study hexagonal Cl adlayers with varying lattice constants ($a_\parallel$) on the jellium with $r_s=2$. The calculation is performed for $a_\parallel=6.0$, 6.5, 7.0, 8.0, and 9.0 bohrs. The calculation procedure is the same as that in Ref. 14, except that a contour integral in the complex energy plane is used in calculating the charge density in order to treat the discrete Cl 3*s* state below the bottom of the continuum jellium band.[16] Given a lattice constant, the only free parameter is the distance between the Cl core and jellium edge. It is chosen as 2.6 bohrs for all $a_\parallel$ as determined by Lang and Williams in the low-Θ limit. Because the Cl valence states are rather localized, the relaxation of the Cl plane with increasing Θ is very small.[17]

The solid and dashed curves in Fig. 1(a) show the calculated work-function change $\Delta\Phi(\Theta)$ and adatom dipole moment $\mu(\Theta)$, which are related by $\Delta\Phi(\Theta)=4\pi\Theta\mu(\Theta)$. $\Delta\Phi(\Theta)$ saturates at higher Θ, and takes a shallow maximum at $a_\parallel=6.5$ bohrs. Correspondingly, $\mu(\Theta)$ decreases monotonically with increasing Θ. The maximum in $\Delta\Phi(\Theta)$ is not experimentally observed. It will be shown later that the adsorption stops before the maximum in $\Delta\Phi(\Theta)$ owing to the rapid decrease in the adsorption energy. $\mu(\Theta)$ stems from the charge redistribution due to chemical interactions between the Cl layer and jellium substrate. Figure 2 shows the contour map of the difference charge $\delta n(\mathbf{r},\Theta)$ in the vertical-cut plane containing Cl atoms at every interval of $a_\parallel$. Here $\delta n(\mathbf{r},\Theta)$ is defined as the charge density of the Cl-covered jellium surface minus the superposed density of the isolated Cl

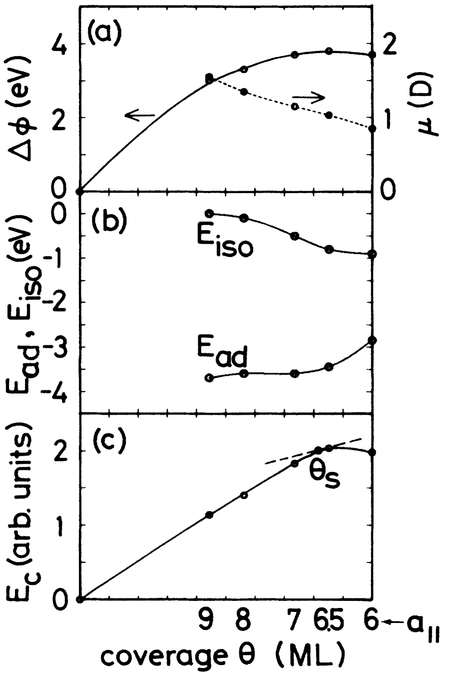

FIG. 1. (a) Calculated work-function change $\Delta\Phi(\Theta)$ and adatom dipole moment $\mu(\Theta)$ for the Cl adlayer on the jellium with $r_s=2$. (b) Total energy per Cl atom for the isolated Cl layer $[E_{\mathrm{iso}}(\Theta)]$, and that for the adlayer $[E_{\mathrm{ad}}(\Theta)]$. (c) Cohesive energy for the whole adlayer, $E_c(\Theta)$. Θ_s denotes the saturation coverage at the zero temperature.

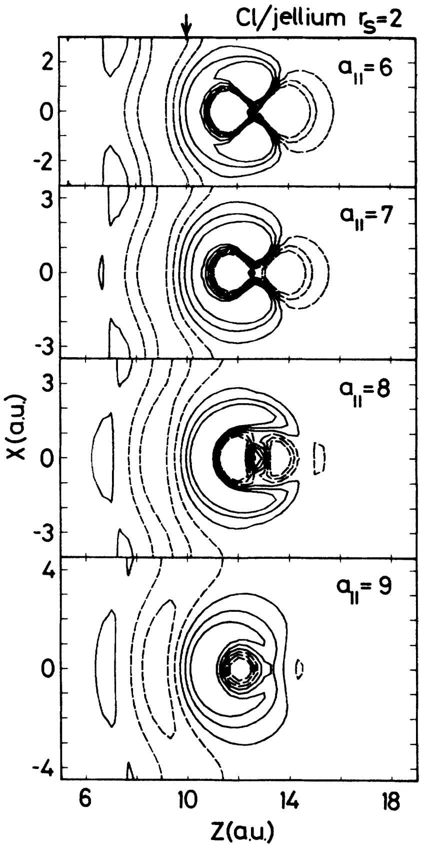

FIG. 2. Contour map of the difference charge for Cl adlayers on the jellium ($r_s=2$) in the vertical-cut planes containing Cl atoms at every interval of $a_{\parallel}$. The jellium edge and Cl sites are indicated by the arrow and solid circles, respectively. The solid (dashed) contours correspond to values of $\delta n(\mathbf{r},\Theta)$ equal to 0.001, 0.003, and 0.005 (-0.001, -0.003, and -0.005) a.u.

layer and clean jellium surface. $\mu(\Theta)$ is given as

$$\mu(\Theta)=N^{-1}\int d\mathbf{r}\, z\,\delta n(\mathbf{r},\Theta)\,,$$

where N is the number of adatoms. The charge increase around a Cl atom and the decrease in the jellium side lead to $\mu(\Theta)$ to increase the work function. The calculated $\delta n(\mathbf{r},\Theta)$ at $a_{\parallel}=9$ bohrs is very similar to that given by Lang and Williams,[13] which implies that the direct interaction among Cl atoms is small at this coverage. If the charge transfer from the jellium to Cl is evaluated by the integrated value of $\delta n(\mathbf{r},\Theta)$ in a sphere around a Cl atom, it decreases from 0.28 to 0.21 electrons (sphere radius $R=3$ bohrs), as $a_{\parallel}$ is reduced from 9 to 6 bohrs.

With increasing Θ, there appears a charge depletion region on the Cl site which has a shape of the p_z orbital and becomes larger. This means that the occupation number of Cl $3p_z$ for the adlayer is smaller at higher Θ than the corresponding one for the isolated Cl layer. On the other hand, as stated above, Cl adatoms are slightly negatively ionized even at higher Θ. Thus the occupation number of Cl $3p_{\parallel}(p_x+p_y)$ for the adlayer must be larger than that for the isolated layer, enough to surpass the deficit in the occupation of Cl $3p_z$. For the isolated Cl layer, the five valence electrons of Cl $3p$ are equally distributed into the x, y, and z components at low Θ. At higher Θ, since the bandwidth of Cl $3p_{\parallel}$ is larger than that of Cl $3p_z$ due to the larger orbital overlap, the $3p_2$ band is fully occupied, and the one hole is accommodated in the $3p_{\parallel}$ band. Namely, the occupation numbers of $3p_z$ and $3p_{\parallel}$ for the isolated Cl layer vary with increasing Θ, from 1.67 to 2.0 electrons, and from 3.33 to 3.0 electrons, respectively.

To examine the origin of the above-mentioned charge relocation on a Cl site, we calculate the adatom density of states (DOS) defined by[18]

$$\rho_a(\epsilon,\Theta)=-\frac{1}{\pi}\int_R d\mathbf{r}\,\mathrm{Im}G(\mathbf{r},\mathbf{r},\epsilon+i\delta,\Theta)\,, \tag{1}$$

where $G(\mathbf{r},\mathbf{r},\epsilon+i\delta,\Theta)$ is the one-electron Green function, and the integration over $\mathbf{r}$ is performed in a Cl atomic sphere with radius R. The solid curves in Fig. 3 show the calculated $\rho_a(\epsilon,\Theta)$. Its $p_{\parallel}$ and p_z components are shown by dash-dotted and dashed curves, respectively. (R is 2.3 bohrs, and δ is 0.2 eV.) The Cl $3s$ band is below the continuum jellium band and is not shown in Fig. 3. $\rho_a(\epsilon,\Theta)$ at $a_{\parallel}=9$ bohrs is again close to that of Lang and Williams,[13] except that the peak of $\rho_a(\epsilon,\Theta)$ is located ~0.5 eV higher than theirs, possibly due to the indirect depolarization effect. The Cl $3p$ resonance is mostly filled, yet the charge transfer to a Cl atom is smaller than unity because the resonance is incomplete.[19] The $3p_z$ orbital has larger overlap with the jellium states than $3p_{\parallel}$. Consequently, Cl

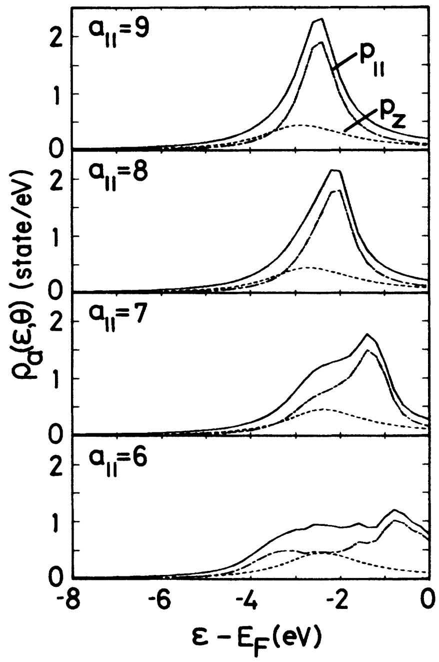

FIG. 3. Adatom density of states $\rho_a(\epsilon,\Theta)$ for a Cl atom on the jellium with $r_s=2$ (solid curves). The dash-dotted and dashed curves show the $p_\parallel$ and p_z components, respectively.

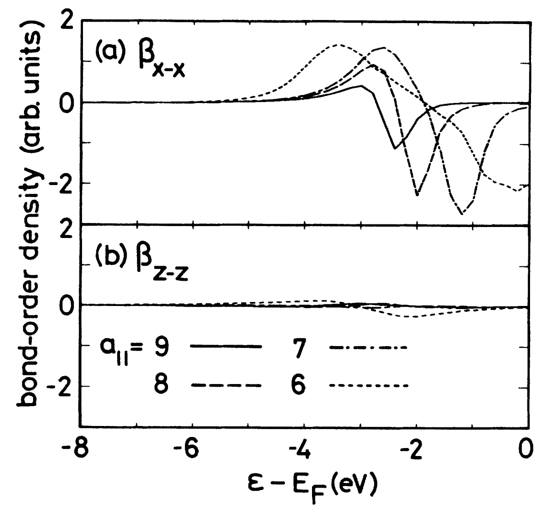

FIG. 4. (a) Bond-order density for the $p_\parallel-p_\parallel$ bonding $\beta_{x-x}(\epsilon,\Theta)$. (b) Bond-order density for the p_z-p_z bonding $\beta_{z-z}(\epsilon,\Theta)$.

$3p_z$ is much broader than Cl $3p_\parallel$ at lower Θ, which implies that Cl $3p_z$ is mainly responsible for the Cl–jellium bonding. Since the overlap between the $3p_z$ orbitals on neighboring Cl sites is small even at higher Θ, the $3p_z$ resonance does not show large Θ dependence. Hence, in contrast to the case of the isolated layer, the occupation number of Cl $3p_z$ for the adlayer is fairly insensitive to Θ. This is the reason why the charge depletion with a shape of the p_z orbital appears in $\delta n(\mathbf{r},\Theta)$ at higher Θ. On the other hand, Cl $3p_\parallel$ shows large Θ dependence. It is sharp at lower Θ, whereas it becomes rapidly wider for $a_\parallel \leq 7$ bohrs, because of the large overlap between the $3p_\parallel$ orbitals on neighboring Cl sites. The occupation of Cl $3p_\parallel$ is fairly constant up to $a_\parallel=7$ bohrs, while it diminishes slightly for higher Θ because part of the $p_\parallel$ DOS starts to spread above the Fermi energy (E_F). The decrease in the Cl $3p_\parallel$ occupation is in accord with the decreasing charge transfer to Cl at higher Θ.

Next, we study the nature of the Cl–Cl bonding. For this purpose, we calculate the p_z-p_z bond-order density $\beta_{z-z}(\epsilon,\Theta)$ defined as

$$\beta_{z-z}(\epsilon,\Theta) = -\frac{1}{\pi}\int_R d\mathbf{r}\int_R d\mathbf{r}'\,\phi_z(\mathbf{r})^*\,\mathrm{Im}G(\mathbf{r},\mathbf{r}',\epsilon+i\delta,\Theta) \times \phi_z(\mathbf{r}'-a_\parallel\mathbf{e}_x)\,, \qquad (2)$$

where $\phi_z=(3/R^3)^{1/2}Y_{10}$ is a p_z orbital normalized in a sphere of radius R, and the integration over $\mathbf{r}$ and $\mathbf{r}'$ is performed in atomic spheres on the neighboring two Cl sites. The p_x-p_x bond-order density $\beta_{x-x}(\epsilon,\Theta)$ is defined in the same way by replacing ϕ_z in Eq. (2) by ϕ_x. Figures 4(a) and 4(b) show the calculated $\beta_{x-x}(\epsilon,\Theta)$ and $\beta_{z-z}(\epsilon,\Theta)$, where their positive and negative signs correspond to bonding and antibonding states with respect to the $p_x-p_x(p_z-p_z)$ bonding, respectively. The amplitude of $\beta_{z-z}(\epsilon,\Theta)$ is much smaller than that of $\beta_{x-x}(\epsilon,\Theta)$, signifying that the interaction of the p_z orbitals on neighboring Cl sites is small even at higher Θ. This is consistent with the Θ-insensitive DOS of Cl $3p_z$. On the other hand, the amplitude of $\beta_{x-x}(\epsilon,\Theta)$ grows rapidly with increasing Θ, corresponding to formation of the wide Cl $3p_\parallel$ band. The lower and upper halves of the Cl $3p_\parallel$ band are bonding and antibonding states, respectively. The wave function of the antibonding state is more localized in Cl spheres than that of the bonding state which has large amplitude also in the Cl–Cl bond region. Therefore the $p_\parallel$ DOS in Fig. 3 becomes asymmetric at higher Θ, having a larger weight in its upper half.

Figure 1(b) shows the total energy per atom for the isolated Cl layer $E_{\mathrm{iso}}(\Theta)$, and that for the adlayer $E_{\mathrm{ad}}(\Theta)$ which is defined as the difference in total energy between the Cl-covered and clean jellium surfaces. [The origin of energy is shifted to $E_{\mathrm{iso}}(\Theta)$ at $a_\parallel=9$ bohrs.] $E_{\mathrm{iso}}(\Theta)$ is lowered with increasing Θ due to the cohesive energy originating from the one hole in the Cl $3p_\parallel$ band as in $\mathrm{Cl_2}$. On the other hand, for the adlayer, because of the charge relocation from Cl $3p_z$ to $3p_\parallel$, as well as due to the small charge transfer from the substrate, more of the antibonding part of the Cl $3p_\parallel$ band is occupied than for the isolated Cl layer, and thus the increase in the bandwidth of Cl $3p_\parallel$ does not lead to the lowering of $E_{\mathrm{ad}}(\Theta)$. According to a total-energy analysis, more than 70% of the rise in $E_{\mathrm{ad}}(\Theta)$ at $a_\parallel=6$ bohrs comes from the increase in the kinetic energy. This is natural because the antibonding states in the Cl $3p_\parallel$ band whose wave function has nodes in the Cl–Cl bond region may have large kinetic energies at high Θ. The mechanism for the energy rise thus resembles the repulsive interaction of closed-shell cores. Because $\mu(\Theta)$ diminishes with increasing Θ, the electrostatic energy due to the Cl-Cl dipole interaction is rather insensitive to Θ at higher Θ and is not crucial for the determination of Θ_s. As the Cl-Cl interaction at $a_\parallel=9$ bohrs is very small for the isolated Cl layer, the adsorption energy of a Cl atom may be estimated as

$$\Delta E_{\mathrm{ad}}(\Theta) = |E_{\mathrm{ad}}(\Theta) - E_{\mathrm{iso}}(a_{\parallel} = 9)| \,.$$

Figure 1(c) shows $E_c(\Theta) = \Theta\Delta E_{\mathrm{ad}}(\Theta)$ which is proportional to the cohesive energy for the whole adlayer. Reflecting the decrease in $\Delta E_{\mathrm{ad}}(\Theta)$, $E_c(\Theta)$ takes a shallow maximum just as for $\Delta\phi(\Theta)$ in Fig. 1(a). At the zero temperature, Θ_s is determined as a point where the slope of $E_c(\Theta)$ equals the binding energy of Cl_2 per atom, 1.25 eV. We obtained $a_{\parallel} = \sim 3.5$ Å for Θ_s. As clarified in the above, the main factor which determines Θ_s is the total-energy rise related with the Cl $3p_{\parallel}$ state. The overlap between $p_{\parallel}$ orbitals on neighboring Cl sites is determined by the Cl-Cl distance independent of the structure or atom species of the substrate. This may be the reason why $a_{\parallel}$ at Θ_s is experimentally fairly constant regardless of the substrate studied.

In summary, we studied the Θ dependence of the electronic structure of Cl adatoms on the jellium substrate by a first-principles calculation. It was found that in accord with experimental observations, the adsorption stops before the maximum in the work-function change due to the rapid decrease in the Cl adsorption energy. Its origin is the kinetic-energy rise on Cl sites which reflects the fact that more of the antibonding part of Cl $3p_{\parallel}$ is occupied as compared with the isolated Cl layer. Nevertheless, the net charge transfer to Cl is not so large because of the decrease in the occupation number of Cl $3p_z$.

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[1] M. Bowker, K. C. Waugh, B. Wolfindale, G. Lamble, and D. A. King, Surf. Sci. **179**, 254 (1987).

[2] W. T. Tysoe and R. M. Lambert, Surf. Sci. **199**, 1 (1988).

[3] D. Westphal and A. Goldmann, Surf. Sci. **131**, 113 (1983).

[4] W. Erley and H. Wagner, Surf. Sci. **66**, 371 (1977).

[5] P. A. Dowben and R. G. Jones, Surf. Sci. **84**, 449 (1979).

[6] J. S. Foord and R. M. Lambert, Surf. Sci. **185**, L483 (1987).

[7] K. K. Kleinherbers and A. Goldmann, Surf. Sci. **154**, 489 (1985); W. Erley, *ibid.* **94**, 281 (1980).

[8] *Physics and Chemistry of Alkali Metal Adsorption*, edited by H. P. Bonzel, A. M. Bradshaw, and G. Ertl (Elsevier, Amsterdam, 1989).

[9] D. R. Hamann, L. F. Mattheis, and H. S. Greenside, Phys. Rev. B **24**, 6151 (1981).

[10] D. W. Bullet, Solid State Commun. **38**, 969 (1981).

[11] B. C. Laskowski and P. S. Bagus, Surf. Sci. **138**, L142 (1984).

[12] Z. Tian, K. Zhang, and X. Xie, Surf. Sci. **163**, 1 (1985).

[13] N. D. Lang and A. R. Williams, Phys. Rev. B **18**, 616 (1978).

[14] H. Ishida, Phys. Rev. B **39**, 5492 (1989).

[15] J. E. Inglesfield, J. Phys. C **14**, 3795 (1981).

[16] b_1, z_j, z_a, b_2, and l in the notation of Ref. 14 are 2, 10, 12.6, 24, and 26 bohrs, respectively. We use the norm-conserving pseudopotential for Cl, and the cutoff energy for the basis function is 12 Ry.

[17] G. M. Lamble, R. S. Brooks, S. Ferrer, D. A. King, and D. Norman, Phys. Rev. B **34**, 2975 (1986).

[18] In Ref. 14, DOS for the clean jellium was subtracted from Eq. (1) in the definition of $\rho_a(\epsilon,\Theta)$.

[19] J. B. Pendry, J. Phys. C **10**, 809 (1977).